

ESTIMATION OF CAKE FORMATION ON MICROFILTRATION MEMBRANE SURFACE USING ZETA POTENTIAL

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Abstract : A simple empirical model with good quantitative prediction of inter-particle and intra-particle distance in a cake layer with respect to ionic strength was developed. The model is an inverse length scale with functions of interaction energy and hydrodynamic factor and it explains that the inter-particle and intra-particle distance in a cake is directly related to the effective size of particles. Particle compressibility with respect to ionic strength was also predicted by the model. The model corroborated very well with experimental results of polystyrene microsphere latex particles microfiltration in a dead end operation. From the results of the model, specific cake resistance could be controlled by the same variables affecting the height of particle energy barrier described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.

Key Words : Inter-particle porosity, Intra-floc porosity, Particle interaction, Specific cake resistance, Ionic strength.

INTRODUCTION

Membrane Fouling is one major limitation to the rapid spread of membrane technology. Fouling is due to the hydraulic resistances offered by the accumulation of particles within membrane surface domain. There are various types of hydraulic resistances but the most prominent with low pressure membranes such as Microfiltration and Ultrafiltration membranes is cake resistance. Cake resistance is due to the accumulation of materials on the membrane surface. It is mathematically defined as the product of cake thickness (δ) and specific cake resistance (α_c). Cake thickness and specific cake resistance are functions of time thus;

cake resistance is a function of time. However, hydrodynamic factors, membrane properties and solution chemistry have been identified as factors affecting specific cake resistance. Several works on the effect of solution chemistry (ionic strength and pH) on specific cake resistance and flux behavior have been done and specific cake resistance with respect to ionic strength was related to the net interaction energy. At high and low interaction energy, porous cake structures have been reported and this has been explained as the effect of dominant repulsive potential¹⁻⁴⁾ and dominant attractive potential⁵⁻¹⁰⁾ respectively.

From these works two types of porosity responsible for low specific cake resistance have been identified. These are the inter-particle porosity and intra-floc porosity. Inter-particle porosity is related to the distance between single

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particles due to the dominating effect of repulsive potential while intra-floc porosity is related to the voids in an aggregate due to the dominating effect of attractive potential.

The objective of this work therefore is to develop an empirical model of particle interaction to predict the inter-particle and intra-floc distance for the control of specific cake resistance with respect to ionic strength of feed stream.

MATERIAL AND METHOD

Membrane Filtration

Flat hydrophilic mixed cellulose ester membranes from Millipore with pore size $0.22 \mu\text{m}$ were used. Membranes were cut to fit the 180 mL Amicon cell unit to give a membrane surface area of 0.003167 m^2 . Unstirred Amicon cell filtration was carried out under a constant pressure of 4 ± 0.1 psi for dead-end operation. Permeate flux was measured by an electronic weighing balance and transmitted to a computer by a data acquisition programme. Monodispersed microsphere latex particles 5,000 series with average particle size $0.3 \mu\text{m}$ packed as aqueous suspensions at 10% solids by weight with refractive index of 1.59 at 589 nm and a density of 1.05 g/cm^3 from Duke Scientific Corporation (USA) were used as modeled colloids. Feed stream was prepared by diluting a known volume ($100 \mu\text{l}$) of $0.3 \mu\text{m}$ latex particle in 1 litre of deionized water with resistivity of $18.2 \text{ M}\Omega\text{-cm}$. Dilute suspension was mixed using magnetic stirrer at 100 rpm and dilution was done after swirling and low ultrasonic bath of the latex particles.

The concentration and pH of the dilute monodispersed particles were kept constant at 5 ppm and 6 ± 0.1 respectively; while the ionic strength was varied. Potassium chloride (KCl) from JUNSEI Corporation (Japan) was used to vary the ionic strength of the solution. The solutions were prepared with deionized water at $18.2 \text{ M}\Omega\text{-cm}$ at a volume ratio of 50%. A schematic diagram of the experimental rig is as shown in Figure 1.

Feed Stream Characteristics

Zeta potential and average particle size of feed stream at various ionic strengths were measured using a Malvern Zetamaster S made by Malvern Instruments Ltd (UK). The Zetamaster is an electrophoresis and particle size analyzer designed to characterize particles of sizes ranging from 1 nm to 5,000 nm by the principle of photon correlation spectroscopy at a fixed angle of 90 degree.

Specific Cake Resistance

Specific cake resistances at various ionic strengths were determined from the basic filtration equation $\frac{t}{V} = \frac{\mu\alpha_c C_b V}{2\Delta P A^2} + \frac{\mu R_m}{\Delta P}$ with $S = \frac{\mu\alpha_c C_b}{2\Delta P A^2}$ where S is the slope of the time-volume ratio versus volume graph. The specific cake resistance determined was correlated with zeta potential and particle size measured from the Zetamaster.

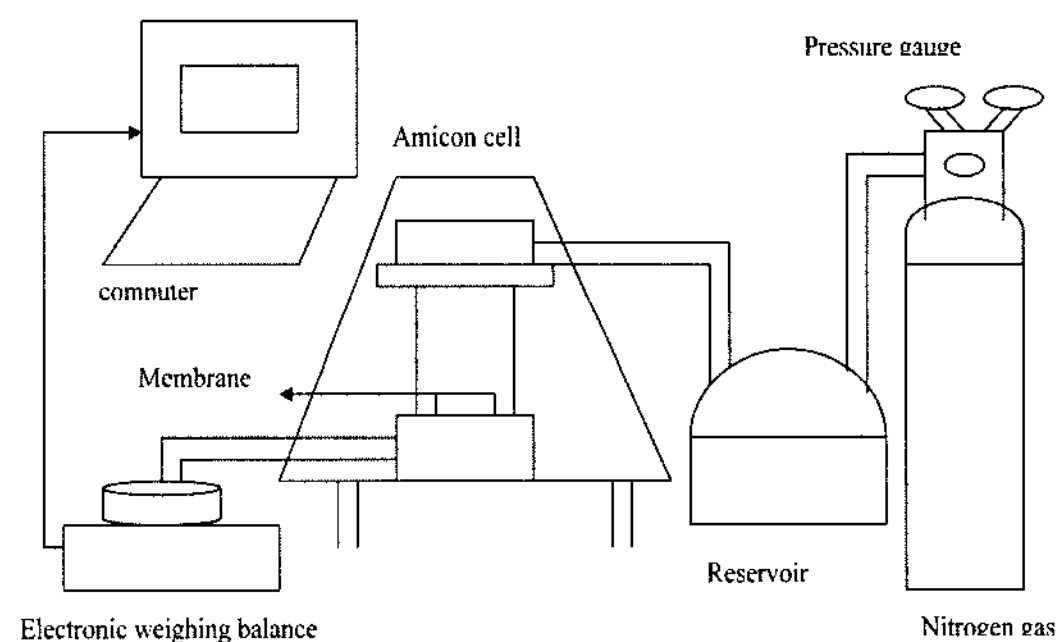


Figure 1. Schematic diagram of dead end Micro-filtration membrane operation

RESULTS AND DISCUSSIONS

Effect of Inter-Particle Porosity and Intra-Floc Porosity on Specific Cake Resistance

Results of experiment as displayed in Figures 2 and 3. revealed that specific cake resistance vary directly with ionic strength (0.0005 M - 0.01 M) where there was no aggregation of particles, but inversely with ionic strength where there was aggregation of particles (0.05 M , 0.1 M , 0.2 M). However, the difference in the specific cake resistance for the various ionic strengths was not quite significant as the curves of Figures 2 and 3

were closely plotted. This is due to the particle size used in the experiment. For a 0.3 μm particle, electrostatic double layer repulsive force is not a dominating force. And electrostatic double layer repulsive force was reported dominant for particles less than 100 nm in size^{3,4}.

The results depicted in Figure 2 and Table 1 explained that at high energy barrier (zeta potential far from isoelectric point) oppositely charged ions from the salt (KCl) screens the double layer thereby decreasing the effective size of particles. And decrease in the effective size implies a decrease in inter-particle distance similarly inter-particle porosity. Thus, for non-aggregated particles, as ionic strength increases, cakes are formed by single dense particles with decreasing inter-particle distances which results in increase in specific cake resistance with increase in ionic strength.

But for aggregated particles the inverse relationship between ionic strength and specific cake resistance was attributed to intra-floc porosity. Since the inter-particle distance continue to decrease with increase in ionic strength and at low energy barrier (zeta potential close to isoelectric point) increase in average particle size was observed this explains that aggregates were formed and these aggregates had voids in them which increased with ionic strength (Table 1), thus a decrease in specific cake resistance with increase in ionic strength as shown in Figure 3.

It was also noted that specific cake resistance was much lower at high ionic strength (0.2 M) than for very low ionic strength (0.0005 M). This could be attributed to the concept of secondary minimum which explains that at low energy barrier; very small inter-particle distance between particles forming aggregates exists. Consequently at high energy barrier cake porosity is a function of

inter-particle distance only, while at low energy barrier cake porosity is a function of inter-particle and intra-particle distance.

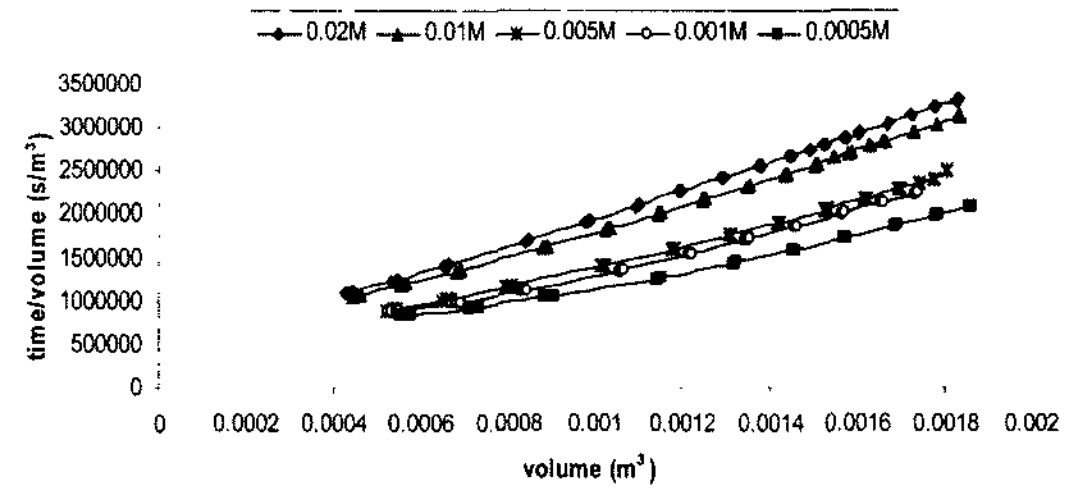


Figure 2. Inverse Flux of Inter-Particle Porosity

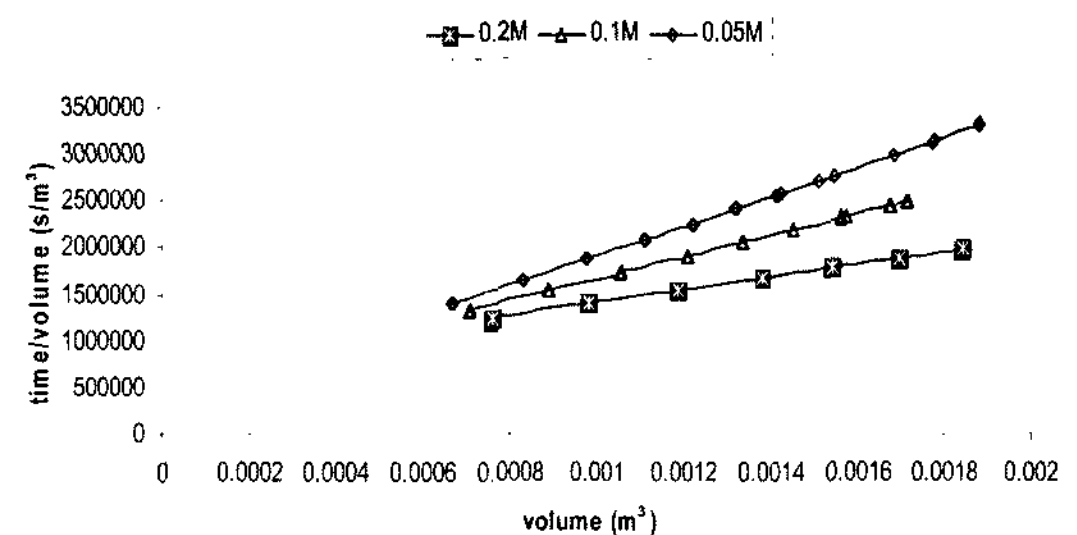


Figure 3. Inverse Flux of Aggregate Porosity

Theoretical Model

Specific cake resistance is a function of inter-particle porosity and aggregate porosity which in turn is dependent on the net interaction energy of particles in solution. And both inter-particle porosity and aggregate porosity could be expressed as a characteristic ratio of an inverse length at any given ionic strength.

Assumptions:

- 1) Colloidal particles are spherical in shape; .
- 2) Ions around colloids are point charges.
- 3) Interaction is between pair of adjacent particles
- 4) Uniform particles with same radius (r), surface potential (φ_s), centre-to-centre distance

Table 1. Relation between Zeta potential and Specific cake resistance

Solution properties	Concentrations (M)								
	0.2	0.1	0.05	0.02	0.01	0.005	0.001	0.0005	
ZP (mV)	-7.57	-9.1	-22.1	-32.2	-45.3	-47.9	-49.6	-50.5	
ap (μm)	0.95	0.58	0.38	0.33	0.33	0.33	0.33	0.33	
α_c (m/kg) $\times 10^{13}$	7.81	13.2	16.9	17.3	16.0	12.6	11.2	9.53	

(s) and Debye-Huckel inverse length (ξ)

5) Thermodynamic equilibrium around the double layer of the particle; this means that change in surface potential of particle is due to the screening effect by electrolyte.

From the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the net interaction energy;

$$\varphi_n = \varphi_R + \varphi_A \dots\dots\dots (1)$$

Where $\varphi_R = 2\pi\epsilon_0 a_P \varphi_o^2 \ln[1 + \exp(-\kappa s)] \dots\dots\dots (2)$

And $\varphi_A = \left(\frac{Aa_P}{ms}\right) \dots\dots\dots (3)$

From equations 2 and 3, it is obvious that the net interaction energy includes so many parameters and it was reported that for a given condition if the Debye inverse length, Hamaker constant and surface potential are well chosen a net energy could be obtained¹¹⁾. However, the size of particles is also a fundamental parameter in describing cake structure and is also a function of the net interaction energy as well and from Coulombs law the net interaction energy is always reduced by permittivity of space and medium. Thus, relating the voids in cake to the net interaction energy, a characteristic ratio (χ) is expressed as;

$$\chi = f(\kappa, \varphi_s, a_P, A_H, \epsilon) \dots\dots\dots (4)$$

From the assumption of thermodynamic equilibrium a change in surface potential is therefore solely an effect of ionic strength and so absolute value of the surface potential will decrease as the ionic strength of the solution increases. But specific cake resistance could also be affected by deposition rate of particles and relating the area space occupied by a particle deposited on a porous media it was stated that it is a function of the square of surface potential¹²⁾. And so a square wise decrease in absolute value of the surface potential will effectively describe the area space made unavailable for particles to occupy which is related to the inter-particle distance. Thus equation 4 could be rewritten as;

$$\chi = f(\kappa, \varphi_s^2, a_P, A_H, \epsilon) \dots\dots\dots (5)$$

From dimensional analysis, therefore;

$$\chi = \theta \kappa^\kappa \zeta^{2\nu} a_P^Z A_H^\gamma \epsilon^w \dots\dots\dots (6)$$

Surface potential (φ_s) is characterized by zeta potential (ζ) which is easier to measure thus; surface potential is replaced by zeta potential. Also, specific cake resistance decreases with increase in porosity, then for dimensional homogeneity, $x \equiv y$, $w \equiv z$ and $v \equiv w \equiv -y$, and θ which is an empirical constant is given the value of unity for simplicity; this therefore, reduces the characteristic ratio to;

$$\chi = \left(\frac{\kappa A_H}{\epsilon \zeta^2 a_P}\right)^\gamma \dots\dots\dots (7)$$

Where y is a dimensionless constant and is inferred to as the hydrodynamic factor since the inter-particle spacing in the bulk solution is always affected by a compressive force from the effect of transmembrane and osmotic pressure on accumulated materials resulting into change in inter-particle or intra-particle distance in the cake. However, inter-particle distance in the bulk solution is not affected by pressure but by ionic strength only consequently, the inter-particle distance in the bulk solution (D_b) from equation 7 is given as;

$$D_b = \left(\frac{\kappa A_H}{\epsilon \zeta^2 a_P}\right)^{-1} \dots\dots\dots (8)$$

And at steady state, hydrodynamic effect with an assumption of a uniform porous structure, inter-or intra-particle distance is given as;

$$D_c = (D_b)^\gamma \dots\dots\dots (9)$$

Equation 8 imply that for the bulk solution, y is always a constant (-1) though not a hydrodynamic factor, but rather explains the inverse relation between ionic strength and the inter-particle

distance. While for equation 9 values of y is given as a range between zero and unity ($0 \leq y \leq 1$) as most materials in water and waste water environment have compressibility factor within this range^{2,13}). Consequently, low pressure corresponds to low value of y , high pressure corresponds to high value of y . Explaining that as particles accumulate on membrane surface, with a compressive force acting against the net interaction energy, inter-particle distance on the cake decreases with increase in transmembrane pressure and an increase in specific cake resistance. This is consistent with the fact that specific cake resistance increases with increase in pressure^{1,2,5}).

However, in relation to ionic strength, for a given transmembrane pressure the value of y also varies. And from the model, for a low specific cake resistance at low ionic strength y should be positive and low while for high ionic strength y should be negative and high. This is because the inter-particle distance is directly related to the absolute value of zeta potential at high energy barrier and inversely related at low energy barrier. Also at high energy barrier small compact, less compressible particles are formed while at low energy barrier large, soft, porous and more compressible aggregates are formed. The variation in the sign of y value explains the difference in particle structure. Consequently, the model predicts two types of porosity, inter-particle porosity and aggregate or intra-floc porosity at low and high ionic strength respectively which is in corroboration with the experimental results.

Verification of y Value

Given that specific cake resistance follows a power law relation with particle-particle interaction, specific cake resistance was plotted against ionic strength with a power law trend as shown in

Figure 4 and 5. The power law trend gave R^2 values of 0.95 and 1 and index value of 0.1559 and -0.5568 respectively. Thus, revealing compressibility factor for low and high energy barrier as predicted by the characteristic ratio. Table 2 also confirms the difference in particle structure at high and low energy barrier as difference in particle structure is one basic explanation for an alteration in the inverse relation between inter-particle distance in the cake (D_c) and ionic strength at low energy. The change in trend is consistent with the low specific cake resistance at high ionic strength. Inter-particle distance in bulk was seen to decrease with increase in ionic strength.

The predicted distance in the bulk solution and cake as shown in Table 2 reveals the good quantitative predictability of the developed empirical model using the energy barrier of the DLVO theory. However, the result of the model for a little increase in average particle size (0.38 μm) at 0.05 M was not in good agreement with the experimental results. This perhaps was due to the high energy barrier at this concentration as indicated by the zeta potential (-22.1 mV).

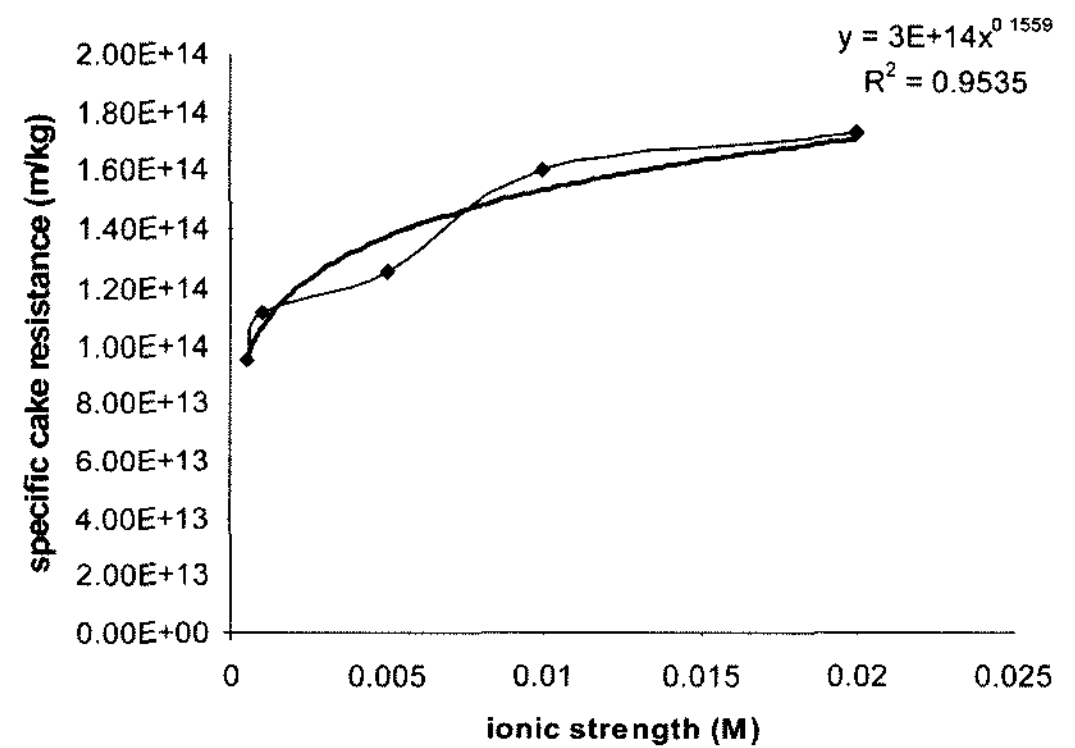


Figure 4. Power law of specific cake resistance for inter-particle porosity

Table 2. Effect of Ionic Strength on Inter-particle and Intra-particle Distance

Solution properties	Concentrations (M)							
	0.2	0.1	0.05	0.02	0.01	0.005	0.001	0.0005
y	-0.5568	-0.5568	-0.5568	0.1559	0.1559	0.1559	0.1559	0.1559
D_b (nm)	0.26	0.33	1.78	5.18	14.6	23.1	55.6	81.3
D_c (nm)	2.12	1.85	0.72	1.29	1.51	1.63	1.87	1.99

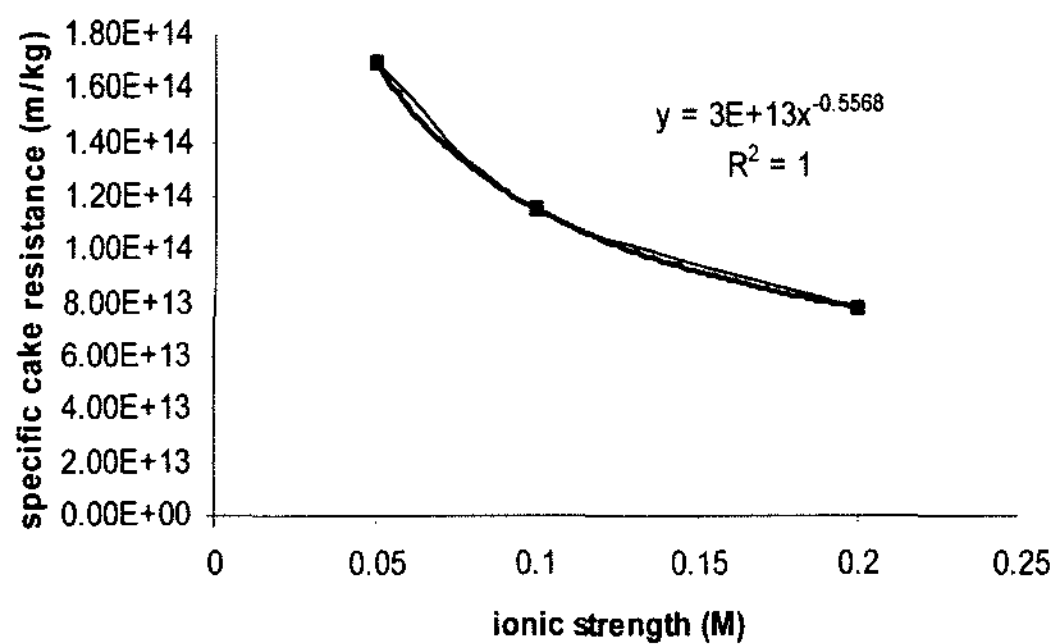


Figure 5. Power law of specific cake resistance for aggregate porosity

CONCLUSIONS

The effect of ionic strength on cake structure was investigated. And at both high and low ionic strengths, low specific cake resistance was possible in direct filtration, with a lower specific cake resistance for the higher ionic strength. A simple empirical model to estimate the void space as inter and intra particle distances was developed and this model corroborated very well with experimental results from the filtration of polystyrene microsphere latex particles. The inclusion of compressibility index in the model estimated the effect of particle structure on compression. From the results of the model, specific cake resistance could be controlled by the same variables affecting the height of particle energy barrier described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.

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Nomenclature

- A membrane area (m^2)
 A_H Harmaker constant (J)
 a_p average particle size (m)
 C_b concentration of feed stream (mg/L)

- D_b inter-particle distance in bulk solution (nm)
 D_c void space in cake (nm)
 m molar mass of particle (g/mole)
 ΔP transmembrane pressure (KPa)
 R_m membrane resistance (m^{-1})
 t time (sec)
 S slope (sec/m^6)
 s centre-to-centre distance (cm)
 V filtrate volume (m^3)
 v, w, x, y, z empirical constants used in dimensional analysis
 α_c specific cake resistance (m/kg)
 χ Characteristic ratio (m^{-1})
 ϵ Permittivity of vacuum and water ($C^2cm^{-1}J^{-1}$)
 Φ_A attractive potential (J)
 Φ_n net interaction potential (J)
 Φ_o surface potential (J)
 Φ_R repulsive potential (J)
 κ Debye-Huckel inverse length (cm^{-1})
 μ Dynamic viscosity of fluid ($Kgm^{-1}sec^{-1}$)
 θ Empirical constant
 ζ Zeta potential (mV)

REFERENCES

1. Kim, A. S., and Hoek, E. M. V. "Cake structure in Dead-end membrane filtration: Monte Carlo Simulations." *Envir. Eng. Sci.*, **19**(6), 373-386 (2002)
2. Chun, M. S., Chung, G. Y., and Kim, J., "On the behavior of the electrostatic colloidal interaction in the membrane filtration of latex suspensions," *J. Membr. Sci.*, **193**, 97-109 (2001)
3. Faibish, R. S., Elimelech, M., and Cohen, Y. "Effect of interparticle electrostatic double layer interactions on permeate flux decline in cross flow membrane filtration of colloids suspensions: An experimental investigation," *J. Colloid Interface Sci.*, **204**, 77-86(1998).
4. Bowen, W. R., and Jenner, F., "Dynamic ultrafiltration model for charged colloidal dispersions; A Wigner-Seitz cell approach,"

- J. Chem. Eng. Sci.*, **50**(11), 1707-1736. (1995)
5. Lee, S. A., Fane, A. G., Amal, R., and Waite, T. D. "The effect of floc size and structure on specific cake resistance and compressibility in dead-end microfiltration," *Sep. Sci. Technol.* **38**(4), 869-887 (2003)
 6. Pikkarainen, A. T., Judd, S. T. Joke, J., and Gillberg, L., "Pre-coagulation of microfiltration of upland surface water," *Water Res.* **38**(2), 455-465(2004).
 7. Kim, A. S., and Yuan, R., "A new model for calculating specific resistance of aggregated colloidal cake layers in membrane filtration processes," *J. Membr. Sci.*, **249**, 89-101 (2005)
 8. Judd, S. J., and Hills, P., "Optimization of combined coagulation and microfiltration for water treatment," *Water Res.*, **35**, 2895-2904 (2001)
 9. Waite, D. T., Schafer, I. A., Fane, and G. A., Heuer, A., "Colloidal fouling of ultra filtration membranes impact of aggregate structure and size," *J. Colloid Interface Sci.* **212**, 264-274 (1999)
 10. Lahousine-Turcard, V., Wiesner, M. Botterro, J. Y., and Malleveialle, J., "Coagulation flocculation with aluminum salts: influence on the filtration efficacy with microporous membranes.," *Water Res.* **26**(5), 695-702 (1992)
 11. Verwey, W. J. E., Overbeek, G., and Th. J., "On the interaction of spherical colloidal particles: Theory of the stability of lyphobic colloids," Dover Publication 1949. pp. 160-161.
 12. Van De Ven, and T. G. M., "Effects of electrolytes polymers and polyelectrolytes on particles deposition and detachment," *J. Colloids Surface*, **39**, 107~126 (1989)
 13. Ho, C., and Zydney, L. A. "A combine pore blockage and cake filtration model for protein fouling during microfiltration.," *J. Colloid Interface Sci.* **232**, 389~399 (2000)